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(54) Title: CATALYTIC PRECIOUS METAL-TREATED CARBON BLACK

(57) Abstract: A catalytic compound comprising an aggregate comprising a carbon phase and a precious metal-containing species phase.



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CATALYTIC PRECIOUS METAL-TREATED CARBON BLACK

The present invention relates to catalytic compounds. More particularly. The present invention relates to catalytic compounds incorporating precious metal-containing carbon blacks, such as platinum-treated or palladium-treated carbon blacks, and products manufactured from such compounds.

Carbon blacks are widely used as pigments, fillers and reinforcing agents in the compounding and preparation of rubber and other elastomeric compounds. Carbon blacks are particularly useful as reinforcing agents in the preparation of elastomeric compounds used in the manufacture of tires. Carbon blacks are also used as conductive supports for electrocatalysts in fuel cells. Moreover it is known that carbon blacks can be used as supports for palladium-iron or palladium-platinum-iron catalysts in the hydrogenation of aromatic nitro compounds.

Carbon blacks are generally produced in a furnace-type reactor by pyrolyzing a hydrocarbon feedstock with hot combustion gases to produce combustion products containing particulate carbon black. Carbon black exists in the form of aggregates. The aggregates, in turn are formed of carbon black particles. However, carbon black particles do not generally exist independently of the carbon black aggregate. Carbon blacks are generally characterized on the basis of analytical properties, including, but not limited to particle size and specific surface area; aggregate size, shape, and distribution; and chemical and physical properties of the surface. The properties of carbon blacks are analytically determined by tests known to the art. For example, nitrogen adsorption surface area (measured by ASTM test procedure D3037-Method A) and cetyl-trimethyl ammonium bromide adsorption value (CTAB) (measured by ASTM test procedure D3765 (09.01), are measures of specific surface

area. Dibutylphthalate absorption of the crushed (CDBP) (measured by ASTM test procedure D3493-86) and uncrushed (DBP) carbon black (measured by ASTM test procedure D2414-93), relates to the aggregate structure.

5 The bound rubber value relates to the surface activity of the carbon black. The properties of a given carbon black depend upon the conditions of manufacture and may be modified, e.g., by altering temperature, pressure, feedstock, residence time, quench temperature, throughput,
10 and other parameters.

It is an object of the present invention to provide catalytic compounds. Particularly, it is an object to provide a catalytic compound incorporating precious metal-treated carbon blacks, such as platinum -treated or
15 palladium-treated carbon blacks.

Additional features and advantages of the present invention will be set forth in part in the description which follows, and in part will be apparent from the description, or may be learned by the practice of the present invention. The
20 objectives and other advantages of the present invention may be realized and obtained by means of the elements and combinations particularly pointed out in the written description and the claims.

To achieve these and other advantages, and in accordance
25 with the purpose of the present invention, as embodied and broadly described herein, the present invention relates to catalytic compounds incorporating precious metal-treated carbon blacks which are aggregates containing at least a carbon phase and a precious metal-containing species phase.

30 Fig. 1 is a schematic view of a portion of one type of carbon black reactor which may be used to produce the treated carbon blacks of the present invention.

The precious metal-treated carbon blacks can be used in catalytic applications. The precious metal-treated carbon blacks are aggregates containing at least a carbon phase and a precious metal-containing species phase. The precious metal-containing species include compounds containing gold, silver, rhenium, platinum, ruthenium, rhodium, palladium, osmium, iridium. The precious metal-containing species include, but are not limited to, oxides of metals. The metal-containing species phase can be distributed through at least a portion of the aggregate and is an intrinsic part of the aggregate. These precious metal-treated carbon blacks may be incorporated into catalytic compounds and can lead to desirable properties. Predominantly, these precious metal treated carbon blacks are used as catalysts for liquid phase hydrogenations other chemical reactions with the exception of or as electrocatalysts in fuel cells.

Precious metal-treated carbon black aggregates do not represent a mixture of discrete carbon black aggregates and discrete precious metal-containing aggregates. Rather, the precious metal-treated carbon black aggregates of the present invention include at least one precious metal-containing region concentrated at or near the surface of the aggregate (but part of the aggregate) or within the aggregate. Thus, as stated earlier, the precious metal-treated carbon black aggregates can be described as aggregates comprising a carbon phase and a precious metal-containing species phase. The aggregates thus contain at least two phases, one of which is carbon and the other of which is a precious metal-containing species. The precious metal-containing species phase that is part of the aggregate is not attached to a carbon black aggregate like a silane coupling agent, but actually is part of the same aggregate as the carbon phase. Further, it is within the bounds of the present invention to have a precious metal-treated carbon black containing more than one type of a precious metal-containing species phase or the precious

metal-treated carbon black can also contain a silicon-containing species phase and/or a boron-containing species phase. For example, the metal-treated carbon black of the present invention can have an aggregate comprising a carbon
5 phase, an platinum-containing species phase, and a palladium-containing species phase. Accordingly, the precious metal-treated carbon black of the present invention can have two or more different types of precious metal-containing species phases and/or additional non-metal
10 species phases.

As indicated above, the aggregate of the present invention can additionally contain a silicon-containing species phase as described in U.S. Patent Applications Serial Nos. 08/446,141; 08/446,142; 08/528,895; and 08/750,017, and PCT
15 Published Application No. WO 96/37547, all incorporated in their entireties by reference.

Such carbon blacks are preferably produced in a furnace carbon black reactor as depicted in Figure 1.

In the furnace carbon black process the oxidative pyrolysis
20 of the carbon black feedstocks is carried out in a reactor lined with refractory materials. In such a reactor three zones may be distinguished, which are arranged in line, one after the other, along the axis of the reactor and have the reaction media flow through them one after the other.

25 The first zone, the so-called combustion zone, essentially comprises the combustion chamber of the reactor. Here a hot process gas is produced through the burning of a fuel, as a rule a hydrocarbon, with a surplus of preheated combustion air or other gases containing oxygen. Today natural gas is
30 used for the most part, but liquid hydrocarbons such as light and heavy heating oil can also be used. The combustion of the fuel usually takes place with a surplus of oxygen. The air surplus here promotes the complete conversion of the fuel and serves to control the carbon

black quality. The fuel is usually fed into the combustion chamber by means of one or more burner lances.

In the second zone of the carbon black reactor, the so-called reaction zone or pyrolysis zone, carbon black
5 formation takes place. For this purpose the carbon black feedstock, in general a so-called carbon black oil, is injected into the stream of the hot process gas and mixed with it. In relation to the quantity of incompletely
10 converted oxygen in the combustion zone, the quantity of hydrocarbons in the reaction zone is in surplus. Hence the formation of carbon black normally sets in here.

Carbon black oil may be injected into the reactor in various ways. For example, an axial oil injection lance or one or more radial oil lances that are arranged on the
15 circumference of the reactor in a plane perpendicular to the direction of flow are suitable. A reactor may have several planes with radial oil lances along the direction of the flow. At the end of the oil lances there are spray nozzles with which the carbon black oil is mixed into the
20 stream of the process gas.

When carbon black oil and gaseous hydrocarbons, such as methane, for example, are used simultaneously as carbon black feedstock, the gaseous hydrocarbons can be injected
25 into the stream of the hot off-gas separately from the carbon black oil by a special set of gas lances.

In the third zone of the carbon black reactor, the so-called separation zone (quench zone), the formation of carbon black is interrupted through the rapid cooling of the process gas containing carbon black. Through this,
30 unwanted after-reactions are avoided. Such after-reactions lead to porous carbon blacks. The cessation of the reaction is generally achieved through spraying in water by means of appropriate spray nozzles. Generally the carbon black reactor has several places along the reactor for spraying

in water or quenching, so that the time that the carbon black stays in the reaction zone may be varied. The residual heat of the process gas is utilized in an attached heat exchanger to preheat the combustion air and the carbon
5 black oil.

The precious metal-treated carbon blacks may be made by introducing a volatilizable metal-containing compound into the carbon black reactor at a point upstream and/or downstream of the quench zone and/or in the quench zone.
10 Useful volatilizable compounds (i.e., the precious metal-containing compounds) include any compound, which is volatilizable at carbon black reactor temperatures. Examples include volatilizable or decomposable compounds containing gold, silver, rhenium, platinum, ruthenium,
15 rhodium, palladium, osmium, iridium and the like. The flow rate of the volatilizable compound will determine the weight percent of precious metal in the treated carbon black. The weight percent of the elemental precious metal (e.g. elemental platinum or palladium) in the treated
20 carbon black generally ranges from about 0.1 % to 99 %, preferably 0.1 % to 25 %, by weight of the aggregate.

The volatilizable compound may be premixed with the carbon black-forming feedstock and introduced with the feedstock into the reaction zone. Alternatively, the volatilizable
25 compound may be introduced to the reaction zone separately from the feedstock injection point. Such introduction may be upstream or downstream from the feedstock injection point, provided the volatilizable compound is introduced upstream and/or downstream from the quench zone and/or in
30 the quench zone. Upon volatilization and exposure to high temperatures in the reactor, the compound decomposes, and reacts with other species in the reaction zone, yielding precious metal-treated carbon black, such that the precious metal, or precious metal-containing species, becomes an
35 intrinsic part of the carbon black.

Besides volatilizable compounds, decomposable metal-containing compounds which are not necessarily volatilizable can also be used to yield the metal-treated carbon black.

- 5 As discussed in further detail below, if the volatilizable compound is introduced substantially simultaneously with the feedstock, the precious metal-treated regions are distributed throughout at least a portion of the carbon black aggregate.
- 10 In a second embodiment, the volatilizable compound is introduced to the reaction zone at a point after carbon black formation has commenced but before the reaction stream has been subjected to the quench. In this embodiment, precious metal-treated carbon black aggregates
- 15 are obtained in which the precious metal-containing species phase is concentrated primarily at or near the surface of the aggregate.

The precious metal-treated carbon black may also be modified to have at least one organic group attached to the

20 precious metal-treated carbon black. Alternatively, or in addition, a mixture of precious metal-treated carbon black and a modified carbon black having at least one attached organic group may be used. In addition, it is within the bounds of the present invention to use a mixture of two or

25 more types of precious metal-treated carbon black in the catalyst.

Methods for attaching organic groups to carbon black and a further discussion of the types of organic groups that can be attached can be found in U.S. Patent Application Serial

30 Nos. 08/356,660; 08/572,525; and 08/356,459, now U.S. Patent No. 5,559,169; and PCT Published Applications Nos. WO 96/18688 and WO 96/18696, the disclosures of which are fully incorporated by reference herein.

One process for attaching an organic group to the carbon black involves the reaction of at least one diazonium salt with a carbon black in the absence of an externally applied current sufficient to reduce the diazonium salt. That is, 5 the reaction between the diazonium salt and the carbon black proceeds without an external source of electrons sufficient to reduce the diazonium salt. Mixtures of different diazonium salts may be used in the process. This process can be carried out under a variety of reaction conditions 10 and in any type of reaction medium, including both protic and aprotic solvent systems or slurries.

In another process, at least one diazonium salt reacts with a carbon black in a protic reaction medium. Mixtures of different diazonium salts may be used in this process. This 15 process can also be carried out under a variety of reaction conditions.

Preferably, in both processes, the diazonium salt is formed in situ. If desired, in either process, the carbon black product can be isolated and dried by means known in the 20 art. Furthermore, the resultant carbon black product can be treated to remove impurities by known techniques. The various preferred embodiments of these processes are discussed below.

These processes can be carried out under a wide variety of 25 conditions and in general are not limited by any particular condition. The reaction conditions must be such that the particular diazonium salt is sufficiently stable to allow it to react with the carbon black. Thus, the processes can be carried out under reaction conditions where the 30 diazonium salt is short lived. The reaction between the diazonium salt and the carbon black occurs, for example, over a wide range of pH and temperature. The processes can be carried out at acidic, neutral, and basic pH.

Preferably, the pH ranges from about 1 to 9. The reaction 35 temperature may preferably range from 0°C to 100°C.

Diazonium salts, as known in the art, may be formed for example by the reaction of primary amines with aqueous solutions of nitrous acid. A general discussion of
5 diazonium salts and methods for their preparation is found in Morrison and Boyd, Organic Chemistry, 5th Ed., pp. 973-983, (Allyn and Bacon, Inc. 1987) and March, Advanced Organic Chemistry; Reactions, Mechanisms, and Structures, 4th Ed., (Wiley, 1992). According to this invention, a
10 diazonium salt is an organic compound having one or more diazonium groups.

The diazonium salt may be prepared prior to reaction with the carbon black or, more preferably, generated in situ using techniques known in the art. In situ generation also
15 allows the use of unstable diazonium salts such as alkyl diazonium salts and avoids unnecessary handling or manipulation of the diazonium salts. In particularly preferred processes, both the nitrous acid and the
 diazonium salt are generated in situ.

A diazonium salt, as is known in the art, may be generated
20 by reacting a primary amine, a nitrite and an acid. The nitrite may be any metal nitrite, preferably lithium nitrite, sodium nitrite, potassium nitrite, or zinc nitrite, or any organic nitrite such as for example isoamyl nitrite or ethyl nitrite. The acid may be any acid,
25 inorganic or organic, which is effective in the generation of the diazonium salt. Preferred acids include nitric acid, HNO₃, hydrochloric acid, HCl, and sulfuric acid, H₂SO₄.

The diazonium salt may also be generated by reacting the primary amine with an aqueous solution of nitrogen dioxide.
30 The aqueous solution of nitrogen dioxide, NO₂/H₂O, provides the nitrous acid needed to generate the diazonium salt.

Generating the diazonium salt in the presence of excess HCl may be less preferred than other alternatives because HCl is corrosive to stainless steel. Generation of the

diazonium salt with $\text{NO}_2/\text{H}_2\text{O}$ has the additional advantage of being less corrosive to stainless steel or other metals commonly used for reaction vessels. Generation using $\text{H}_2\text{SO}_4/\text{NaNO}_2$ or $\text{HNO}_3/\text{NaNO}_2$ are also relatively non-corrosive.

- 5 In general, generating a diazonium salt from a primary amine, a nitrite, and an acid requires two equivalents of acid based on the amount of amine used. In an in situ process, the diazonium salt can be generated using one equivalent of the acid. When the primary amine contains a
- 10 strong acid group, adding a separate acid may not be necessary. The acid group or groups of the primary amine can supply one or both of the needed equivalents of acid. When the primary amine contains a strong acid group, preferably either no additional acid or up to one
- 15 equivalent of additional acid is added to a process of the invention to generate the diazonium salt in situ. A slight excess of additional acid may be used. One example of such a primary amine is para-aminobenzenesulfonic acid (sulfanilic acid).
- 20 In general, diazonium salts are thermally unstable. They are typically prepared in solution at low temperatures, such as $0-5^\circ\text{C}$, and used without isolation of the salt. Heating solutions of some diazonium salts may liberate nitrogen and form either the corresponding alcohols in
- 25 acidic media or the organic free radicals in basic media.

However, the diazonium salt need only be sufficiently stable to allow reaction with the carbon black. Thus, the process can be carried out with some diazonium salts otherwise considered to be unstable and subject to

30 decomposition. Some decomposition processes may compete with the reaction between the carbon black and the diazonium salt and may reduce the total number of organic groups attached to the carbon black. Further, the reaction may be carried out at elevated temperatures where many

35 diazonium salts may be susceptible to decomposition.

Elevated temperatures may also advantageously increase the solubility of the diazonium salt in the reaction medium and improve its handling during the process. However, elevated temperatures may result in some loss of the diazonium salt
5 due to other decomposition processes.

Reagents can be added to form the diazonium salt in situ, to a suspension of carbon black in the reaction medium, for example, water. Thus, a carbon black suspension to be used may already contain one or more reagents to generate the
10 diazonium salt and the process accomplished by adding the remaining reagents.

Reactions to form a diazonium salt are compatible with a large variety of functional groups commonly found on organic compounds. Thus, only the availability of a
15 diazonium salt for reaction with a carbon black limits the processes of the invention.

The processes can be carried out in any reaction medium which allows the reaction between the diazonium salt and the carbon black to proceed. Preferably, the reaction
20 medium is a solvent-based system. The solvent may be a protic solvent, an aprotic solvent, or a mixture of solvents. Protic solvents are solvents, like water or methanol, containing a hydrogen attached to an oxygen or nitrogen and thus are sufficiently acidic to form hydrogen
25 bonds. Aprotic solvents are solvents which do not contain an acidic hydrogen as defined above. Aprotic solvents include, for example, solvents such as hexanes, tetrahydrofuran (THF), acetonitrile, and benzonitrile. For a discussion of protic and aprotic solvents see Morrison
30 and Boyd, Organic Chemistry, 5th Ed., pp. 228-231, (Allyn and Bacon, Inc. 1987).

The processes are preferably carried out in a protic reaction medium, that is, in a protic solvent alone or a mixture of solvents which contains at least one protic

solvent. Preferred protic media include, but are not limited to water, aqueous media containing water and other solvents, alcohols, and any media containing an alcohol, or mixtures of such media.

5 The reaction between a diazonium salt and a carbon black can take place with any type of carbon black, for example, in fluffy or pelleted form. In one embodiment designed to reduce production costs, the reaction occurs during a process for forming carbon black pellets. For example, a
10 carbon black product of the invention can be prepared in a dry drum by spraying a solution or slurry of a diazonium salt onto a carbon black. Alternatively, the carbon black product can be prepared by pelletizing a carbon black in the presence of a solvent system, such as water, containing
15 the diazonium salt or the reagents to generate the diazonium salt in situ. Aqueous solvent systems are preferred. Accordingly, another embodiment provides a process for forming a pelletized carbon black comprising the steps of: introducing a carbon black and an aqueous
20 slurry or solution of a diazonium salt into a pelletizer, reacting the diazonium salt with the carbon black to attach an organic group to the carbon black, and pelletizing the resulting carbon black having an attached organic group. The pelletized carbon black product may then be dried using
25 conventional techniques.

In general, the processes produce inorganic by-products, such as salts. In some end uses, such as those discussed below, these by-products may be undesirable. Several
30 possible ways to produce a carbon black product without unwanted inorganic by-products or salts are as follows:

First, the diazonium salt can be purified before use by removing the unwanted inorganic by-product using means known in the art. Second, the diazonium salt can be generated with the use of an organic nitrite as the
35 diazotiazation agent yielding the corresponding alcohol

rather than an inorganic salt. Third, when the diazonium salt is generated from an amine having an acid group and aqueous NO_2 , no inorganic salts are formed. Other ways may be known to those of skill in the art.

5 In addition to the inorganic by-products, a process may also produce organic by-products. They can be removed, for example, by extraction with organic solvents. Other ways of obtaining products without unwanted organic by-products may be known to those of skill in the art and include washing
10 or removal of ions by reverse osmosis.

The reaction between a diazonium salt and a carbon black forms a carbon black product having an organic group attached to the carbon black. The diazonium salt may contain the organic group to be attached to the carbon
15 black. It may be possible to produce the carbon black products of this invention by other means known to those skilled in the art.

The organic group may be an aliphatic group, a cyclic organic group, or an organic compound having an aliphatic
20 portion and a cyclic portion. As discussed above, the diazonium salt employed in the processes can be derived from a primary amine having one of these groups and being capable of forming, even transiently, a diazonium salt. The organic group may be substituted or unsubstituted, branched
25 or unbranched. Aliphatic groups include, for example, groups derived from alkanes, alkenes, alcohols, ethers, aldehydes, ketones, carboxylic acids, and carbohydrates. Cyclic organic groups include, but are not limited to, alicyclic hydrocarbon groups (for example, cycloalkyls,
30 cycloalkenyls), heterocyclic hydrocarbon groups (for example, pyrrolidinyl, pyrrolinyl, piperidinyl, morpholinyl, and the like), aryl groups (for example, phenyl, naphthyl, anthracenyl, and the like), and heteroaryl groups (imidazolyl, pyrazolyl, pyridinyl,
35 thienyl, thiazolyl, furyl, indolyl, and the like). As the

stearic hindrance of a substituted organic group increases, the number of organic groups attached to the carbon black from the reaction between the diazonium salt and the carbon black may be diminished.

- 5 When the organic group is substituted, it may contain any functional group compatible with the formation of a diazonium salt. Preferred functional groups include, but are not limited to, R, OR, COR, COOR, OCOR, carboxylate salts such as COOLi, COONa, COOK, $\text{COO}^-\text{NR}_4^+$, halogen, CN,
- 10 NR_2 , SO_3H , sulfonate salts such as SO_3Li , SO_3Na , SO_3K , $\text{SO}_3^-\text{NR}_4^+$, OSO_3H , OSO_3^- salts, $\text{NR}(\text{COR})$, CONR_2 , NO_2 , PO_3H_2 , phosphonate salts such as PO_3HNa and PO_3Na_2 , phosphate salts such as OPO_3HNa and OPO_3Na_2 , $\text{N}=\text{NR}$, NR_3^+X^- , PR_3^+X^- , S_kR , SSO_3H , SSO_3^- salts, $\text{SO}_2\text{NRR}'$, SO_2SR , SNRR' , SNQ , SO_2NQ , CO_2NQ , S-(1,4-
- 15 piperazinediyl)-SR, 2-(1,3-dithianyl) 2-(1,3-dithiolanyl), SOR , and SO_2R . R and R', which can be the same or different, are independently hydrogen, branched or unbranched $\text{C}_1\text{-C}_{20}$ substituted or unsubstituted, saturated or unsaturated hydrocarbon, e.g., alkyl, alkenyl, alkynyl,
- 20 substituted or unsubstituted aryl, substituted or unsubstituted heteroaryl, substituted or unsubstituted alkylaryl, or substituted or unsubstituted arylalkyl. The integer k ranges from 1-8 and preferably from 2-4. The anion X^- is a halide or an anion derived from a mineral or
- 25 organic acid. Q is $(\text{CH}_2)_w$, $(\text{CH}_2)_x\text{O}(\text{CH}_2)_z$, $(\text{CH}_2)_x\text{NR}(\text{CH}_2)_z$, or $(\text{CH}_2)_x\text{S}(\text{CH}_2)_z$, where w is an integer from 2 to 6 and x and z are integers from 1 to 6.

A preferred organic group is an aromatic group of the formula $\text{A}_y\text{Ar}-$, which corresponds to a primary amine of the

30 formula A_yArNH_2 . In this formula, the variables have the following meanings: Ar is an aromatic radical such as an aryl or heteroaryl group. Preferably, Ar is selected from the group consisting of phenyl, naphthyl, anthracenyl, phenanthrenyl, biphenyl, pyridinyl, benzothiadiazolyl, and

35 benzothiazolyl; A is a substituent on the aromatic radical

independently selected from a preferred functional group described above or A is a linear, branched or cyclic hydrocarbon radical (preferably containing 1 bis 20 carbon atoms), unsubstituted or substituted with one or more of those functional groups; and y is an integer from 1 to the total number of -CH radicals in the aromatic radical. For instance, y is an integer from 1 to 5 when Ar is phenyl, 1 to 7 when Ar is naphthyl, 1 to 9 when Ar is anthracenyl, phenanthrenyl, or biphenyl, or 1 to 4 when Ar is pyridinyl.

10 In the above formula, specific examples of R and R' are $\text{NH}_2\text{-C}_6\text{H}_4\text{-}$, $\text{CH}_2\text{CH}_2\text{-C}_6\text{H}_4\text{-NH}_2$, $\text{CH}_2\text{-C}_6\text{H}_4\text{-NH}_2$, and C_6H_5 .

Another preferred set of organic groups which may be attached to the carbon black are organic groups substituted with an ionic or an ionizable group as a functional group.

15 An ionizable group is one which is capable of forming an ionic group in the medium of use. The ionic group may be an anionic group or a cationic group and the ionizable group may form an anion or a cation.

Ionizable functional groups forming anions include, for example, acidic groups or salts of acidic groups. The organic groups, therefore, include groups derived from organic acids. Preferably, when it contains an ionizable group forming an anion, such an organic group has a) an aromatic group and b) at least one acidic group having a pKa of less than 11, or at least one salt of an acidic group having a pKa of less than 11, or a mixture of at least one acidic group having a pKa of less than 11 and at least one salt of an acidic group having a pKa of less than 11. The pKa of the acidic group refers to the pKa of the organic group as a whole, not just the acidic substituent.

20 25 30 35

More preferably, the pKa is less than 10 and most preferably less than 9. Preferably, the aromatic group of the organic group is directly attached to the carbon black. The aromatic group may be further substituted or unsubstituted, for example, with alkyl groups. More

preferably, the organic group is a phenyl or a naphthyl group and the acidic group is a sulfonic acid group, a sulfinic acid group, a phosphonic acid group, or a carboxylic acid group. Examples of these acidic groups and their salts are discussed above. Most preferably, the organic group is a substituted or unsubstituted sulfophenyl group or a salt thereof; a substituted or unsubstituted (polysulfo)phenyl group or a salt thereof; a substituted or unsubstituted sulfonaphthyl group or a salt thereof; or a substituted or unsubstituted (polysulfo)naphthyl group or a salt hereof. A preferred substituted sulfophenyl group is hydroxysulfophenyl group or a salt thereof.

Specific organic groups having an ionizable functional group forming an anion (and their corresponding primary amines) are p-sulfophenyl (p-sulfanilic acid), 4-hydroxy-3-sulfophenyl (2-hydroxy-5-amino-benzenesulfonic acid), and 2-sulfoethyl (2-aminoethanesulfonic acid). Other organic groups having ionizable functional groups forming anions can also be used.

Amines represent examples of ionizable functional groups that form cationic groups. For example, amines may be protonated to form ammonium groups in acidic media. Preferably, an organic group having a amine substituent has a pK_b of less than 5. Quaternary ammonium groups ($-NR_3^+$) and quaternary phosphonium groups ($-PR_3^+$) also represent examples of cationic groups. Preferably, the organic group contains an aromatic group such as a phenyl or a naphthyl group and a quaternary ammonium or a quaternary phosphonium group. The aromatic group is preferably directly attached to the carbon black. Quaternized cyclic amines, and even quaternized aromatic amines, can also be used as the organic group. Thus, N-substituted pyridinium compounds, such as N-methyl-pyridyl, can be used in this regard. Examples of organic groups include, but are not limited to,

$(C_5H_4N)C_2H_5^+$, $C_6H_4(NC_5H_5)^+$, $C_6H_4COCH_2N(CH_3)_3^+$, $C_6H_4COCH_2(NC_5H_5)^+$, $(C_5H_4N)CH_3^+$, and $C_6H_4CH_2N(CH_3)_3^+$.

An advantage of the carbon black products having an attached organic group substituted with an ionic or an ionizable group is that the carbon black product may have increased water dispersibility relative to the corresponding untreated carbon black. Water dispersibility of a carbon black product increases with the number of organic groups attached to the carbon black having an ionizable group or the number of ionizable groups attached to a given organic group. Thus, increasing the number of ionizable groups associated with the carbon black product should increase its water dispersibility and permits control of the water dispersibility to a desired level. It can be noted that the water dispersibility of a carbon black product containing an amine as the organic group attached to the carbon black may be increased by acidifying the aqueous medium.

Because the water dispersibility of the carbon black products depends to some extent on charge stabilization, it is preferable that the ionic strength of the aqueous medium be less than 0.1 molar. More preferably, the ionic strength is less than 0.01 molar.

When such a water dispersible carbon black product is prepared, it is preferred that the ionic or ionizable groups be ionized in the reaction medium. The resulting product solution or slurry may be used as is or diluted prior to use. Alternatively, the carbon black product may be dried by techniques used for conventional carbon blacks. These techniques include, but are not limited to, drying in ovens and rotary kilns. Overdrying, however, may cause a loss in the degree of water dispersibility.

In addition to their water dispersibility, carbon black products having an organic group substituted with an ionic

or an ionizable group may also be dispersible in polar organic solvents such as dimethylsulfoxide (DMSO), and formamide. In alcohols such as methanol or ethanol, use of complexing agents such as crown ethers increases the dispersibility of carbon black products having an organic group containing a metal salt of an acidic group.

Aromatic sulfides encompass another group of preferred organic groups. Carbon black products having aromatic sulfide groups are particularly useful in rubber compositons. These aromatic sulfides can be represented by the formulas $\text{Ar}(\text{CH}_2)_q\text{S}_k(\text{CH}_2)_r\text{Ar}'$ or $\text{A}-(\text{CH}_2)_q\text{S}_k(\text{CH}_2)_r\text{Ar}''$ wherein Ar and Ar' are independently substituted or unsubstituted arylene or heteroarylene groups, Ar'' is an aryl or heteroaryl group, k is 1 to 8 and q and r are 0-4. Substituted aryl groups would include substituted alkylaryl groups. Preferred arylene groups include phenylene groups, particularly p-phenylene groups, or benzothiazolylene groups. Preferred aryl groups include phenyl, naphthyl and benzothiazolyl. The number of sulfurs present, defined by k preferably ranges from 2 to 4. Preferred carbon black products are those having an attached aromatic sulfide organic group of the formula $-(\text{C}_6\text{H}_4)-\text{S}_k-(\text{C}_6\text{H}_4)-$, where k is an integer from 1 to 8, and more preferably where k ranges from 2 to 4. Particularly preferred aromatic sulfide groups are bis-para- $(\text{C}_6\text{H}_4)-\text{S}_2-(\text{C}_6\text{H}_4)-$ and para- $(\text{C}_6\text{H}_4)-\text{S}_2-(\text{C}_6\text{H}_5)$. The diazonium salts of these aromatic sulfide groups may be conveniently prepared from their corresponding primary amines, $\text{H}_2\text{N}-\text{Ar}-\text{S}_k-\text{Ar}'-\text{NH}_2$ or $\text{H}_2\text{N}-\text{Ar}-\text{S}_k-\text{Ar}''$. Preferred groups include dithiodi-4,1-phenylene, tetrathiodi-4,1-phenylene, phenyldithiopenylene, dithiodi-4,1-(3-chlorophenylene), $-(4-\text{C}_6\text{H}_4)-\text{S}-\text{S}-(2-\text{C}_7\text{H}_4\text{NS})$, $-(4-\text{C}_6\text{H}_4)-\text{S}-\text{S}-(4-\text{C}_6\text{H}_4)-\text{OH}$, $-6-(2-\text{C}_7\text{H}_3\text{NS})-\text{SH}$, $-(4-\text{C}_6\text{H}_4)-\text{CH}_2\text{CH}_2-\text{S}-\text{S}-\text{CH}_2\text{CH}_2-(4-\text{C}_6\text{H}_4)-$, $-(4-\text{C}_6\text{H}_4)-\text{CH}_2\text{CH}_2-\text{S}-\text{S}-\text{S}-\text{CH}_2\text{CH}_2-(4-\text{C}_6\text{H}_4)-$, $-(2-\text{C}_6\text{H}_4)-\text{S}-\text{S}-(2-\text{C}_6\text{H}_4)-$, $(3-\text{C}_6\text{H}_4)-\text{S}-\text{S}-(3-\text{C}_6\text{H}_4)-$, $-6-(\text{C}_6\text{H}_3\text{N}_2\text{S})$, $-6-(2-\text{C}_7\text{H}_3\text{NS})\text{S}-\text{NRR}'$ where RR' is $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$, $-(4-\text{C}_6\text{H}_4)-\text{S}-\text{S}-\text{S}-\text{S}-(4-\text{C}_6\text{H}_4)-$, $-(4-\text{C}_6\text{H}_4)-\text{CH}=\text{CH}_2$, $-(4-\text{C}_6\text{H}_4)-\text{S}-\text{SO}_3\text{H}$, $-(4-\text{C}_6\text{H}_4)-\text{SO}_2\text{NH}-(4-\text{C}_6\text{H}_4)-\text{S}-\text{S}-$

- (4-C₆H₄)-NHSO₂-(4-C₆H₄)-, -6-(2-C₇H₃NS)-S-S-2-(6-C₇H₃NS)-, -
 (4-C₆H₄)-S-CH₂-(4-C₆H₄)-, -(4-C₆H₄)-SO₂-S-(4-C₆H₄)-, -(4-C₆H₄)-
 CH₂-S-CH₂-(4-C₆H₄)-, -(3-C₆H₄)-CH₂-S-CH₂-(3-C₆H₄)-, -(4-C₆H₄)-
 CH₂-S-S-CH₂-(4-C₆H₄)-, -(3-C₆H₄)-CH₂-S-S-CH₂-(3-C₆H₄)-, -(4-
 5 C₆H₄)-S-NRR' where RR' is -CH₂CH₂OCH₂CH₂-, -(4-C₆H₄)-SO₂NH-
 CH₂CH₂-S-S-CH₂CH₂-NHSO₂-(4-C₆H₄)-, -(4-C₆H₄)-2-(1,3-
 dithianyl;), and -(4-C₆H₄)-S-(1,4-piperizinediyl)-S-(4-
 C₆H₄)-.

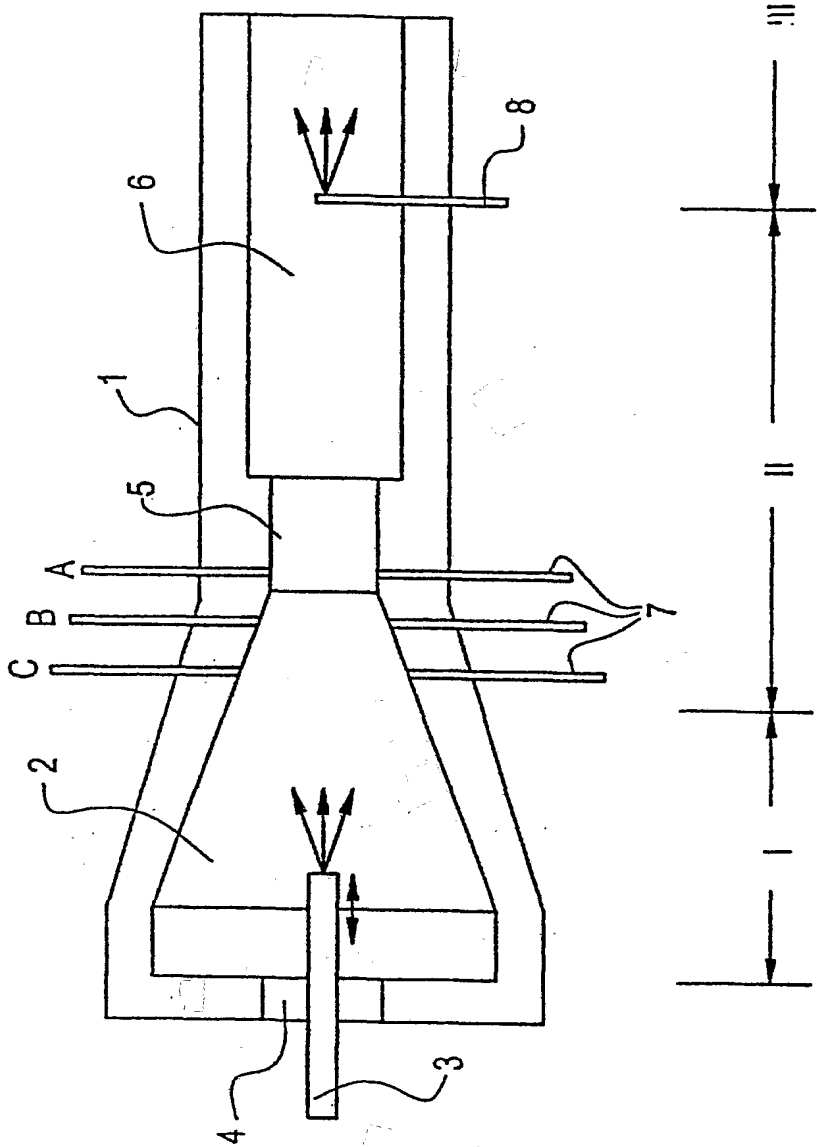
- Another preferred set of organic groups which may be
 10 attached to the carbon black are organic groups having an
 aminophenyl, such as (C₆H₄)-NH₂, (C₆H₄)-CH₂(C₆H₄)-NH₂, (C₆H₄)-
 SO₂-(C₆H₄)-NH₂. Preferred organic groups also include
 aromatic sulfides, represented by the formulas Ar-S_n-Ar' or
 Ar-S_n-Ar'', wherein Ar and Ar' are independently arylene
 15 groups, Ar'' is an aryl and n is 1 to 8. Methods for
 attaching such organic groups to carbon black are discussed
 in U.S. patent applications serial nos. 08/356,660,
 08/572,525, and 08/356,459, the disclosures of which are
 fully incorporated by reference herein.

Claims:

1. A catalytic compound comprising an aggregate comprising a carbon phase and a precious metal-containing species phase.
- 5 2. The catalytic compound of claim 1, wherein said metal-containing species comprises a gold-containing species phase, a silver-containing species phase, a rhenium-containing species phase, a platinum-containing species phase, a ruthenium-containing species phase, a rhodium-
10 containing species phase, a palladium-containing species phase, a osmium-containing species phase, an iridium-containing species phase or mixtures thereof.
3. The catalytic compound of claim 1, wherein said
15 precious metal-containing species phase exists primarily at the surface of the aggregate.
4. The catalytic compound of claim 1, wherein said precious metal-containing species phase is distributed throughout the aggregate.
5. The catalytic compound of claim 1, wherein said
20 precious metal-containing species phase is oxidized.
6. The catalytic compound of claim 1, further comprising a carbon black having an organic group attached thereto.
7. The catalytic compound of claim 1, wherein said
25 aggregate further comprises a silicon-containing species phase.
8. The catalytic compound of claim 1, wherein said aggregate comprises at least two different precious metal-containing species phases.
9. A method of making an catalytic compound comprising
30 introducing at least one volatilizable or decomposable

- precious metal-containing compound into a reactor along with a carbon black feedstock or during the formation of carbon black at a sufficient temperature to decompose or volatilize said compound and form an aggregate comprising a carbon phase and at least one precious metal-containing species phase.
10. The method of claim 23, wherein said volatilizable or decomposable precious metal-containing compound comprises a compound containing gold, silver, rhenium, platinum, ruthenium, rhodium, palladium, osmium, iridium or mixtures thereof.

FIG. 1



INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/00313

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J23/38 B01J23/54 B01J23/89 C09C1/56 H01M4/86
H01M4/88

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C09C H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 767 036 A (HEINZ GERHARD ET AL) 16 June 1998 (1998-06-16) column 1, line 10 - line 28 column 3, line 35 - line 46 column 4, line 36 - line 37 column 4, line 47 - line 49 column 6, line 29 - line 33 column 12, line 19 - line 24 claims 1-7 ---	1-4
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

Z document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US 4 186 110 A (JALAN VINOD M ET AL) 29 January 1980 (1980-01-29) column 1, line 5 - line 23 column 1, line 42 - line 56 column 2, line 58 - line 63 column 4, line 29 - line 53 column 5, line 22 - column 6, line 29 example 1 claims 1, 5, 6	1-5
Y	column 5, line 4 - line 9	6-10
Y	WO 98 47971 A (CABOT CORP) 29 October 1998 (1998-10-29) page 1, line 20 - line 22 page 6, line 5 - page 16, line 5 page 16, line 30 - page 26, line 25 claims 25-57, 68	6-10
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		WO 9842778 A1	01-10-1998
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